

POLARIZATION AND COVALENCY IN ALKALI-TETRALIDE CLUSTERS.

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Abstract

In this paper we discuss the structure of A_4M_4 alkali(= A)-tetralide (= M) (= group 14) clusters. Without polarization these polyions consist of a central tetralide tetrahedron with each face capped by an alkali ion. We show that ionic polarization can lead to quite different cluster structures by breaking up of the tetralide tetrahedron into pairs M_2 , and it can even destroy covalent bonds in these clusters. Consequences for the structure of the solid, liquid and amorphous phase are discussed.

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1 INTRODUCTION.

In this paper we present results of model calculations on the atomic structure of A_4M_4 clusters, where A is an alkali: Li, Na, K, Rb, Cs, and M a group 14 atom, also called tetralides: Si, Ge, Sn, Pb. We use a simple Hückel-type approximation for the electronic structure and an ionic model for the interionic Coulomb and polarization interactions.

A study of the atomic structure of this type of clusters is of importance for the understanding of the structural and electronic properties of these clusters, but also for the associated crystalline, amorphous and liquid phase. The corresponding solid equiatomic AM compounds can roughly be divided – based on their crystallographic structure – into three groups (for a review of the structure see [1, 2]). A group which contains a clear three dimensional network of three-fold coordination on the M sublattice: LiSi and LiGe. Another group which contains charged covalently bonded M_4 tetrahedra. Also in this configuration M has a three-fold coordination. And finally the group in which one suspects only weak M–M bonds, LiSn and LiPb. There are other structures possible for the tetralide sublattice: for example in some alkaline-earth ditetralides one finds layer structures. We will not discuss these compounds in the present paper.

The basis for an interpretation of the structure of these compounds is that in these compounds one electron is transferred from the alkali to the tetralide. The local structure of the M sublattice of the first two groups can be rationalized using the Zintl [3] concept: because one electron is transferred from the alkali to the tetralide, the valence electron configuration of the M^- tetralide ion of group 14 is equivalent to that of group 15: the pnictides: P, As, Sb and Bi. This M^- ion acts as a pseudo element with chemical bonding characteristics equal to those of the next group. This is indeed what one observes.

We have explained the difference between the compounds with and without tetrahedra as due to the size of the alkali [4] (to be referred to as paper I). When the alkali ion becomes too small it is not able to separate the tetrahedra and the bonds within and between tetrahedra become the same. In that situation the system may choose another structure for the M sublattice, leading – in our particular case – to the other two different structure types observed for the LiM compounds. The large difference between the structures of LiSi and LiGe on the

one hand and the LiSn and LiPb structures on the other hand is probably due to a difference in covalent M–M bonding, which is much larger in the first than in the second case. We have tried to quantify this but only succeeded in a qualitative way [5].

In I we already noted the importance of polarization in determining the local structure in these type of systems. However polarization is difficult to take into account in the models we used. In order to calculate the contribution of the electronic structure to the total energy, we approximated the atomic structure of the tetralide sublattice by some type of pseudolattice in which angles and next-nearest neighbour distances are not well defined. Therefore we decided to study smaller units, which are a representation of the solid: neutral A_4M_4 units. Such units were postulated by [6] to explain neutron diffraction data on liquid alloys of these compounds. Sabounji has observed that these units seem to rotate rather free at high temperatures in the solid phase without going into a liquid phase: the so-called rotor phase [7]. There are many more indications for the presence of such rather stable entities in the liquid, from thermodynamic data [8], from the amorphous phase [9], and from an analysis of neutron diffraction experiments [10, 11]. For a recent review of the field see for example [12, 13].

In recent molecular dynamics simulations of the liquid phase of these systems, using the Car-Parrinello method [14] – [19], one finds all kind of aggregates on the tetralide sublattice, pairs, broken tetrahedra, chains, and mixtures of chains and tetrahedra. In an analysis one finds however a clear indication for preferred three-fold coordination with in many cases a peak around 60° in the three-particle correlation function of the tetralide partial structure factor.

Recently, theoretical studies of the structure and stability of these tetralide clusters have been published [20] using the local density approximation. These studies done by the Valladolid group are most pertinent to our study, however they neglect the core polarization, which we will show is very important in determining the atomic structure of these systems.

2 THEORY.

We use a rather simple model to calculate and minimize the ground state energy with respect to the interatomic distances and to determine the stable atomic structures of these clusters. We

use a Hückel type tight-binding model, using Harrison's new parametrization scheme [21, 22], with nonorthogonal orbitals to calculate the electronic structure of these clusters. On the alkali as well as the tetralide we only take into account valence s and p orbitals. The so-called peripheral s state correction in this new scheme is taken into account as a perturbation.

To this we add the Born repulsion between two atoms a distance R_{12} apart, which we approximate by

$$F(\rho_1 + \rho_2) \exp((R_1^0 + R_2^0 - R_{12})/(\rho_1 + \rho_2)). \quad (1)$$

The Born radius R_i^0 of atom i is fitted so that the experimental and calculated interatomic distances agree. The range of the Born repulsion of atom i is taken as $\rho_i = R_i^0/18.6$. We tried other values, but this did not have a large effect on our results. We set the prefactor $F = 0.5e^2$, where e is the electronic charge.

The van der Waals interaction is approximated by C/R^6 , where we took the van der Waals coefficient $C = \alpha$, i.e. equal to the polarization of the ion.

The ionic Coulomb interactions are calculated with the full ionic charges. For ionic solids this is a good approximation for the lattice energy. Whether this approximation also holds for these clusters, which are partially ionic, is questionable. The dipolar energy includes the dipole-electric field, dipole-dipole and dipole self energy. The latter should be taken into account because all dipoles are induced. The (maximum) polarizabilities are taken from Fraga [23], and are denoted by α_F . In order to calculate the polarization energy one has to minimize the contributions involving the induced dipole moments. This leads to a finite set of linear equations in the induced dipole moment.

In order to find the minimum energy for the atomic configuration of a cluster, we use a simple simplex scheme. The starting configuration of each system is some random configuration. From the electronic structure calculation we find a nearly complete transfer of one electron from the alkali to the tetralide. For large polarizabilities ($\alpha > 0.7\alpha_F$) the system often becomes frozen into some state with one very short AM bond, leading to a large induced dipole moment on the M ion. The length of the dipole moment – based on one electron – far exceeds the diameter of the atom or ion. In this case the dipolar energy exceeds all other energies. The largest polarizability we can take for the tetralide without encountering this problem is about 0.75 to

0.8 times the Fraga values. For larger values the cluster always finds a configuration with a very large polarization energy. We also performed calculations using the Fraga values and varying the ionic charges. We found that only ionic charges up to about 0.8 give stable clusters. For larger ionic charges we encounter the same problems as reported above for the case of large polarizabilities.

3 RESULTS AND DISCUSSION.

In order to test the reliability of this scheme for our clusters we calculated the binding energy and vibration energy of the neutral M_2 and M_4 , and the charged M_4^{4-} clusters. In the case of the neutral clusters we have to consider only the electronic hybridization energy and the Born repulsion. The Born radius is fitted to the interatomic distances observed in their crystalline structure, using the charged M_4^{4-} clusters. Using this Born radius we obtain good agreement with experiment for the interatomic distance, binding energy, and vibration frequency of the neutral clusters M_2 and M_4 . These results will be published elsewhere together with a more detailed account of the model [24]. So we are rather confident that the covalent bonding is rather well described within this model, at least for the interatomic distances for these clusters. We have applied this model also to other neutral clusters like MX_4 , where X is a halide, and to clusters of pnictides. We find good agreement with experiment (interatomic distances, binding energy and vibration frequency) whenever available. Results on these neutral systems will be published elsewhere.

We varied the polarizability from zero to approximately 0.7 times the Fraga values. The results of these calculations are displayed in table 1. We find the following three stable atomic configurations for these clusters using this model approach: The Normal Double Tetrahedron (NDT), which consists of a central M_4 tetrahedron with the four A ions capped outside on its four faces. The Face Centered Tetrahedron (FCT), where the four A ions are approximately near the center of the four faces of the M_4 tetrahedron. And a configuration consisting of two pairs of M_2 clusters, bridged by the four A ions. We found other atomic configurations in which the simplex got stuck, like a M_4 square, with two A ions on each side, a double pyramid, with

three short and three long bonds of the M_4 subcluster, and an A ion in the base plane (three long bonds). The binding energy of the latter configurations is some eV above the ground state configuration.

We find that without polarization all systems have a NDT ground state. Molina et al [20] find the same atomic configuration for Li_4Pb_4 and Na_4Pb_4 clusters. Turning on the polarization however causes a separation of these clusters in three groups: The group where the ground state remains a NDT configuration up to 0.6 times the Fraga polarizability: these are all the K_4M_4 , Rb_4M_4 , and Cs_4M_4 clusters, the group where there is a transition to the FCT state, without – or nearly without – an intermediate state with M_2 pairs in the Li_4Sn_4 , Li_4Pb_4 , Na_4Sn_4 and Na_4Pb_4 clusters, and the group where there is a clear intermediate state with pairs, before the cations move to approximately the center of the faces of the M_4 tetrahedron (Li_4Si_4 , Li_4Ge_4 , Na_4Si_4 , Na_4Ge_4). In figure 1 we illustrate these structures for the Li_4Si_4 cluster: for small polarizability the NDT structure has the lowest energy, for intermediate polarizability the structure with two Si_2 pairs is most stable, and for large polarizability of Si the FCT structure has lowest energy.

Let us next try to explain these structural transitions. When the polarization is turned on, the cluster can and wants to increase the polarization contribution to the total energy, however this will cost Coulomb as well as hybridization energy. When the alkali ions are outside the M_4 tetrahedron, the electric field on the M ion is rather small, as the fields of the alkali and the tetrahedron nearly cancel. The way to gain polarization energy is to move the alkalis from far outside to more near the faces of the M_4 tetrahedra, however this will cause an increase of the interatomic distances of the M_4 tetrahedron. When the covalent bonding is large like in the case of Si and Ge, an intermediate state can be created, in which the Si or Ge form pairs, with a relative large covalent bonding energy. Further increase of the polarization causes also a break up of these M_2 pairs, and we finally have a FCT configuration, where the covalent bonding between the M ions is weakened, although in the case of Si and Ge it still gives a relative large contribution to the total binding energy.

We note that when we increase the polarization the M–M bond length in general decreases, except in the case Li_4Pb_4 , Li_4Sn_4 , Na_4Pb_4 . This decrease is caused by the fact that the electric field increases with decreasing bondlength, thereby increasing the polarization energy

contribution to the binding energy. The M–M bondlength for two values ($\alpha = 0$, and $.5\alpha_F$) of the polarizability are given in table 1. The increase of the M–M distance when the polarization is turned on is the precursor for the NDT \rightarrow FCT transition.

From our model calculations we find rather natural the often observed tetrahedral atomic configuration for Li and less often observed for Na [25, 26]. This configuration is especially stable for counter-ions with a large polarizability, like Pb^- . This atomic configuration of the Li_4 cluster is – in the systems studied here – not due to direct covalent bonding between the Li ions, but due polarization effects. The Li p levels are too high in energy to participate in bonding. The M_4 have become essentially noninteracting, this subcluster is in this limit (FCT) not stable on its own account.

Finally, in figure 2 we present results on the calculation of the atomic structure of Cs_nPb_4 clusters for $n = 1, 2, 3$. For $n = 1$ we find a capped tetrahedron, for $n = 2$ a square of Pb, with a Cs on each square face, and for $n = 3$ we find a three-capped tetrahedron. Such clusters have also been studied by the Valladolid group [20] for Li–Pb and Na–Pb. Our structures differ appreciably from theirs for $n = 1$ and for $n = 2$. However for $n = 3$ our structure for Cs–Pb is very similar to their structures. In their calculation they did not take into account the core polarization. Furthermore the local density approximation using pseudopotentials is probably less adequate to describe the electronic and therefore the atomic structure of clusters with strong ionic bonding. It would be of interest to study alkali-rich clusters, especially for Si and Ge.

Let us now discuss the observed crystalline structures based on the results of the present calculations. First we note that the electric fields due to the ions in the condensed phase can never attain such large values as one finds in a cluster. However, starting with the NDT configuration without polarization, also the condensed phase can lower its energy by changing the bonding in the M sublattice. Such changes in bonding are more easily accomplished in a liquid or amorphous state than in a crystalline solid. In the latter case periodicity imposes restrictions on the local structure. However a liquid exists only at high temperatures and we [8] have seen that at these temperature notwithstanding the relative high binding energy of the clusters, entropic effects cause these clusters to dissociate. At very low temperature in

the amorphous phase we expect these clusters to exist as rather stable entities, localizing the valence electrons in their covalent bonds [9]. This is actually the interpretation of the lack of the peak in the resistivity for $\text{Na}_x\text{Pb}_{1-x}$ as a function of x in the liquid state: there are no M_4^{4-} tetrahedra to capture the conduction electrons in its bonds. That is, the $\text{NDT} \rightarrow \text{FCT}$ transition in NaPb occurs on melting. In the amorphous phase one observes such a peak.

Systems where such a transition away from the NDT configuration is possible with the lowest fraction of the polarizability are the LiM systems. One notices also that LiSi and LiGe have a strong tendency to form pairs, while LiSn has a small tendency and LiPb has a direct transition from the NDT to the FCT configuration. This could explain why in the solid state the LiSi and LiGe form a three-dimensional network, while LiSn and LiPb do not. So, based on polarization, we have a rather clear separation between the LiM systems and the other A_4M_4 systems and within the LiM systems between LiSi and LiGe on the one side and LiSn and LiPb on the other side.

The hardest bonds are the M_4 bonds, while the MA bonds are much weaker. So by applying pressure one will shorten MA bonds, thereby increasing the polarization energy contribution, leading to a break up of the M_4 tetrahedron. We expect that one of the easiest systems to transform from the NDT to the FCT-like structure is the NaPb system: the electric fields, causing the polarization break up of the covalent MM bonds, are relatively large, while the covalent interactions in the M_4 tetrahedron are relatively weak. So under pressure we expect it to transform from a system with tetrahedra to one without.

4 CONCLUSIONS.

Based on our model calculation we conclude that the ionic polarization cannot be neglected in the calculation of the atomic structure of polyions, with partially ionic bonding, i.e. cluster consisting of atoms with a large difference in electronegativity. We also have seen that polarization energy gain can break up even relatively strong covalent bonds like in the case of LiSi and LiGe . Clearly, effects due to polarization are in these cluster opposite to those of covalent bonding: covalent bonding favors a NDT structure, while polarization favors a FCT structure.

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Table 1: Stable atomic configurations found for the A_4M_4 clusters, as a function of polarizability.

NDT: Double tetrahedron with the alkalis capped outside on the four faces of the tetralide tetrahedron.

FCT: The same as NDT, but with each alkali capped near the center of the one of the four faces.

Pairs: Two tetralide pairs, bridged by alkali ions.

The value of the fraction of the maximum polarization (α_F) where the transition takes place from one cluster structure to another is indicated above the arrows. The error is about ± 0.02 . Below the arrows we give the interatomic M–M distance (in Å) for zero polarizability and for a finite value of the polarizability. The polarizability is given in parenthesis. For details see the main text.

		Si	Ge	Sn	Pb
		$R^0 = 1.2; \alpha = 7.27$	$R^0 = 1.31; \alpha = 7.51$	$R^0 = 1.49; \alpha = 10.8$	$R^0 = 1.62; \alpha = 12.4$
Li	$R^0 = 1.25$ $\alpha = 0.003$	NDT $\xrightarrow{0.31}$ pairs $\xrightarrow{0.56}$ FCT 2.60(0.0);2.53(0.25)	NDT $\xrightarrow{0.35}$ pairs $\xrightarrow{0.48}$ FCT 2.71(0.0);2.66(0.25)	NDT $\xrightarrow{0.31}$ pairs $\xrightarrow{0.39}$ FCT 3.09(0.0);3.13(0.25)	NDT $\xrightarrow{0.34}$ FCT 3.36(0.0);3.49(0.25)
Na	$R^0 = 1.35$ $\alpha = 0.155$	NDT $\xrightarrow{0.55}$ pairs $\xrightarrow{0.80}$ FCT 2.65(0.0);2.49(0.25)	NDT $\xrightarrow{0.51}$ pairs $\xrightarrow{0.70}$ FCT 2.80(0.0);2.66(0.25)	NDT $\xrightarrow{0.44}$ pairs $\xrightarrow{0.46}$ FCT 3.15(0.0);3.48(0.25)	NDT $\xrightarrow{0.37}$ FCT 3.43(0.0);3.45(0.25)
K	$R^0 = 1.59$ $\alpha = 0.947$	NDT $\xrightarrow{>0.75}$ pairs/FCT 2.87(0.0);2.42(0.5)	NDT $\xrightarrow{>0.75?}$ pairs/FCT 3.00(0.0);2.57(0.5)	NDT $\xrightarrow{0.72}$ pairs/FCT 3.34(0.0);2.98(0.5)	NDT $\xrightarrow{0.60}$ pair $\xrightarrow{0.63}$ FCT 3.61(0.0);3.33(0.5)
Rb	$R^0 = 1.71$ $\alpha = 1.65$	NDT $\xrightarrow{>0.75}$ pairs/FCT 3.03(0.0);2.42(0.5)	NDT $\xrightarrow{>0.75}$ pairs/FCT 3.15(0.0);2.57(0.5)	NDT $\xrightarrow{>0.75}$ pairs/FCT 3.48(0.0);2.9(0.53)	NDT $\xrightarrow{0.74}$ pairs 3.73(0.0);3.31(0.5)
Cs	$R^0 = 1.82$ $\alpha = 3.08$	NDT $\xrightarrow{>0.75}$ pairs 3.19(0.0);2.41(0.5)	NDT $\xrightarrow{>0.75}$ pairs 3.40(0.0);2.57(0.5)	NDT $\xrightarrow{>0.75}$ pairs 3.63(0.0);2.97(0.5)	NDT $\xrightarrow{0.81}$ FCT 3.87(0.0);3.30(0.5)

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Figure Captions

Figure 1: The atomic structure of Li_4Si_4 clusters as a function of the polarizability: A $\alpha = 0$ (NDT); B $0.4\alpha_F$ (two pairs); C $0.55\alpha_F$ (FCT); α_F is the value for the polarizability from [23].

Figure 2: The atomic structure of the Cs_nPb_4 clusters for $n = 1, 2, 3$ clusters with polarizability: $0.25\alpha_F$; α_F is the value for the polarizability from [23].



